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DEPARTMENT OF GEOPHYSICAL SCIENCES
SCHOOL OF SCIENCES AND HEALTH PROFESSIONS
OLD DOMINION UNIVERSITY
NORFOLK, VIRGINIA

Technical Report GSTR-79-8

EVALUATION OF ATMOSPHERIC TRACE CONSTITUENT SENSORS OPERATING FROM REMOTE SPACE AND AIRBORNE PLATFORMS

By

Estelle Condon and Earl C. Kindle

Principal Investigator: Earl C. Kindle

Final Report
Period ending June 13, 1979

Prepared for the
National Aeronautics and Space Administration
Langley Research Center
Hampton, Virginia 23665

Under
Research Grant NSG 1394
Henry G. Reichle, Jr., Technical Monitor
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By

Estelle Condon[1] and Earl C. Kindle[2]

INTRODUCTION

Increased urbanization and industrialization have raised many questions concerning man's impact on the atmosphere of Earth. The effect of emitting tons of gases into the atmosphere each year from the burning of fossil fuels is as yet undetermined. The effect of changes in agricultural methods on the atmosphere with the increased use of fertilizers, pesticides, and irrigation is also unknown. Since the basic chemistry of the Earth's atmosphere is not well defined, the ultimate influence of man's activities on the natural atmospheric processes and climate may not be fully assessed.

To gain a better understanding of these processes and the basic chemistry of the Earth's lower atmosphere, a program has been conducted by Old Dominion University (ODU) in conjunction with the NASA/Langley Research Center (LaRC) to study atmospheric trace gas concentrations. This study is part of a larger effort conducted by NASA/LaRC to determine the global distribution of carbon monoxide using both direct and remote measurement techniques.

To achieve regional and global scale survey measurements of the CO distribution, the remote sensor is being developed by NASA/LaRC. The remote sensor, a gas filter correlation radiometer (GFCR), has been accepted for flight aboard Space Shuttle (ref. 1), and as such will provide a global midtropospheric measurement for CO for a 4-day period between 40°N and 40°S latitude during late 1980. The experiment is

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unique, and represents the first attempt to measure a tropospheric gas on such a wide scale in so short a time frame. Direct measurements, as described herein, have been carried out by ODU.

PROGRAM HISTORY

Under NASA research grant NSG 1127, a laboratory gas analysis system was developed specifically to make trace level measurements of carbon monoxide (see Appendix). To assure that the data collected with this system are correctly aligned with other established methods for making these measurements, an intercalibration study was initiated in 1977 and expanded in 1978. Samples were exchanged in 1978 with Dr. Leroy Heidt of the National Center for Atmospheric Research in Boulder, Colorado, with Dr. Wolgang Seiler of the Max Planck Institute in Germany, and lastly with Dr. R. Rasmussen of the Oregon Graduate Center. The final results of the data comparisons have now all been reported. The calibration gas was analyzed by the various participating laboratories and found to contain 1.28 ppm CO. The intercalibration should now be repeated at concentrations more representative of the ambient CO levels usually measured by these experimenters.

Under NASA research grants NSG 1127 and NSG 1394, ODU participated in a number of field programs. In 1976 measurements were made in the Southern Lake Michigan Basin. Results of this experiment were discussed in a paper presented at the Fourth Joint Conference on Sensing of Environmental Pollutants in New Orleans, Louisiana (ref. 2).

In January 1978 samples were collected at 25°, 35°, and 45°N for profile data to study the variation in concentrations of CO and CH_4 as a function of altitude and latitude in continental air over the eastern seaboard of the United States. The experiment was repeated in August 1978 to determine if there were seasonally dependent variations in the CO and CH_4 concentrations. The results of the January experiment have been submitted for publication to Geophysical Research Letters. Comparisons will be made between the August data and the January data, and these results will also be submitted for literature publication.

Significant results on one of the major field experiments conducted by the program were presented at the Fourth Joint Conference on Sensing of Environmental Pollutants, New Orleans, Louisiana, November 1977 in a paper by J.C. Casas, E.P. Condon, and S.A. Campbell entitled "Procedures Utilized for Obtaining Direct and Remote Atmospheric Carbon Monoxide Measurements over the Lower Lake Michigan Basin in August of 1976." A special technique for the measurement of trace gases was developed under the program and is described in detail in the Appendix.

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1. Reichle, H.G. et al.: Measurement of Air Pollutant from Satellites Experiment (MAPS). Proposal to NASA Headquarters for OFT-2 Space Shuttle Mission, Dec. 1976.

2. Casas, J.C.; Condon, E.P., and Campbell, S.A.: Procedures Utilized for Obtaining Direct and Remote Atmospheric Carbon Monoxide Measurements over the Lower Lake Michigan Basin in August of 1976. Fourth Joint Conference on Sensing of Environmental Pollutants (New Orleans, LA), Nov. 1977.

APPENDIX

A MEASUREMENT SYSTEM FOR THE ATMOSPHERIC TRACE GASES CH_4 AND CO

DEPARTMENT OF PHYSICS AND GEOPHYSICAL SCIENCES
SCHOOL OF SCIENCES AND HEALTH PROFESSIONS
OLD DOMINION UNIVERSITY
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A MEASUREMENT SYSTEM FOR THE ATMOSPHERIC TRACE GASES CH_4 AND CO

By

Estelle P. Condon

Interim Report

Prepared for the
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Henry G. Reichle, Jr. Technical Monitor
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Submitted by the
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ABSTRACT

A system for measuring ambient clean air levels of the atmospheric trace gases methane and carbon monoxide is described. The analytical method consists of a gas chromatographic technique that incorporates sample preconcentration with catalytic conversion of CO to CH_4 and subsequent flame ionization detection of these gases. The system developed has sufficient sensitivity and repeatability to make the precise measurements required to establish concentration profiles for CO and CH_4 in the planetary boundary layer. A discussion of the bottle sampling program being conducted to obtain the samples for the concentration profiles is also presented.

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A MEASUREMENT SYSTEM FOR THE ATMOSPHERIC TRACE GASES CH_4 AND CO

By

Estelle Condon[1]

BACKGROUND

Investigations into the behavior and variability of trace gases in the atmosphere are necessary to gain a better understanding of the basic chemistry of the Earth's atmosphere. Accurate measurements of the trace gas constituents are necessary before the sources, transport routes, reactions, and sinks of the gases in nature can be defined. Also, determining the distribution of certain pollutant gases is a major problem in obtaining environmental statistics that are needed for effective air quality control. Currently, very little nonurban data are available on the distributions of trace gases, particularly their vertical distributions.

Studies to determine trace gas concentration profiles in the planetary boundary layer were begun under grant NSG 1127. As a result of these studies, a measurement system incorporating gas chromatography was developed that has sufficient sensitivity and repeatability to make the precise measurements required to establish concentration profiles for carbon monoxide and methane. This report presents a description of that system and its operation.

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INTRODUCTION

This report will describe in detail the procedures and equipment used to measure ambient clean air levels of carbon monoxide (CO) and methane (CH_4). The apparatus and analysis procedure for the measurement system are modeled after that used by John W. Swinnerton, et al., of the Naval Research Laboratory and described in references 1, 2, 3, and 4. The description herein will include the analytical system with its individual components, the calibration of that system, and data reduction. A section on sampling and bottle samples is also included to provide a complete discussion of the total process necessary to obtain a concentration profile for CO and CH_4.

The measurement system hardware consists of several systems as shown schematically in the block diagram of figure 1: sample/calibration injection system; preconcentration system; a modified laboratory gas chromatograph; and the data recording system. Figure 2 is a photograph of the system as operated in the laboratory.

Since CO exists in the troposphere at only about 0.1 to 0.2 parts per million by volume (ppmv), the air samples must be preconcentrated for proper operation of the gas chromatograph detector. In this system, the preconcentration is accomplished by using a cold trap operated at -77° C. After preconcentration of the sample, the gas chromatograph is used to separate the particular gases of interest. The gas chromatograph detector output signal is then plotted on a strip chart recorder where the peak area is computed for each individual component by the digital integrator. Each step in this process, as well as a thorough description of all hardware, will be explained in the following sections of this paper.

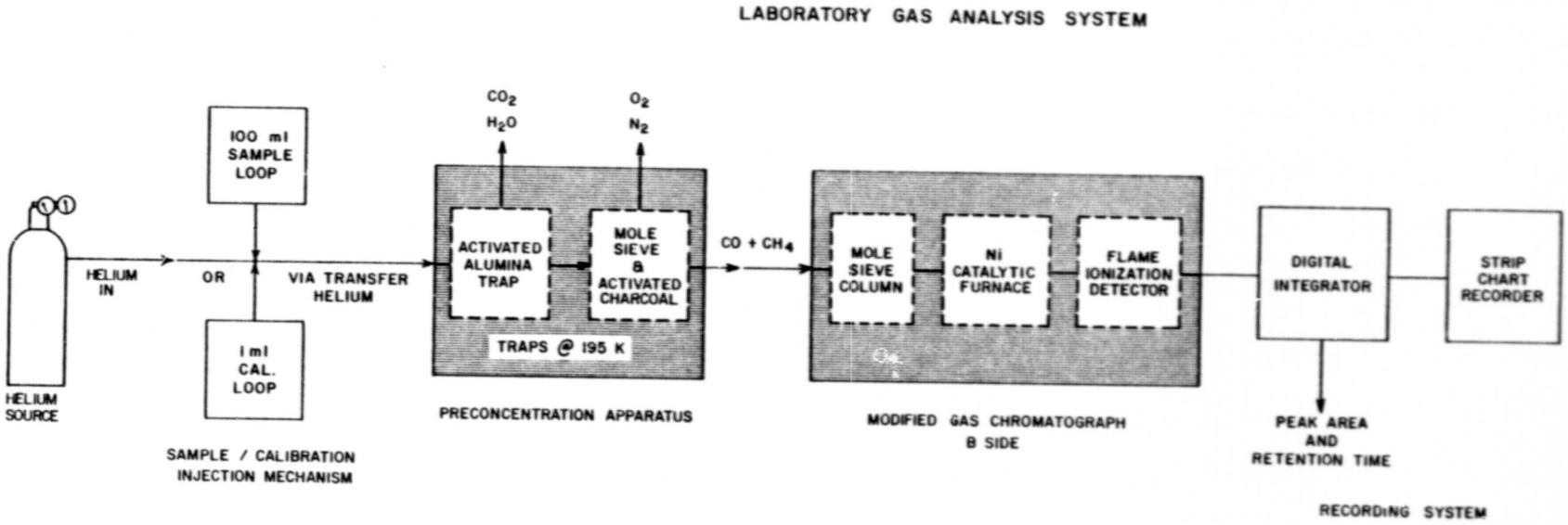

Figure 1. Flow diagram of the analysis system.

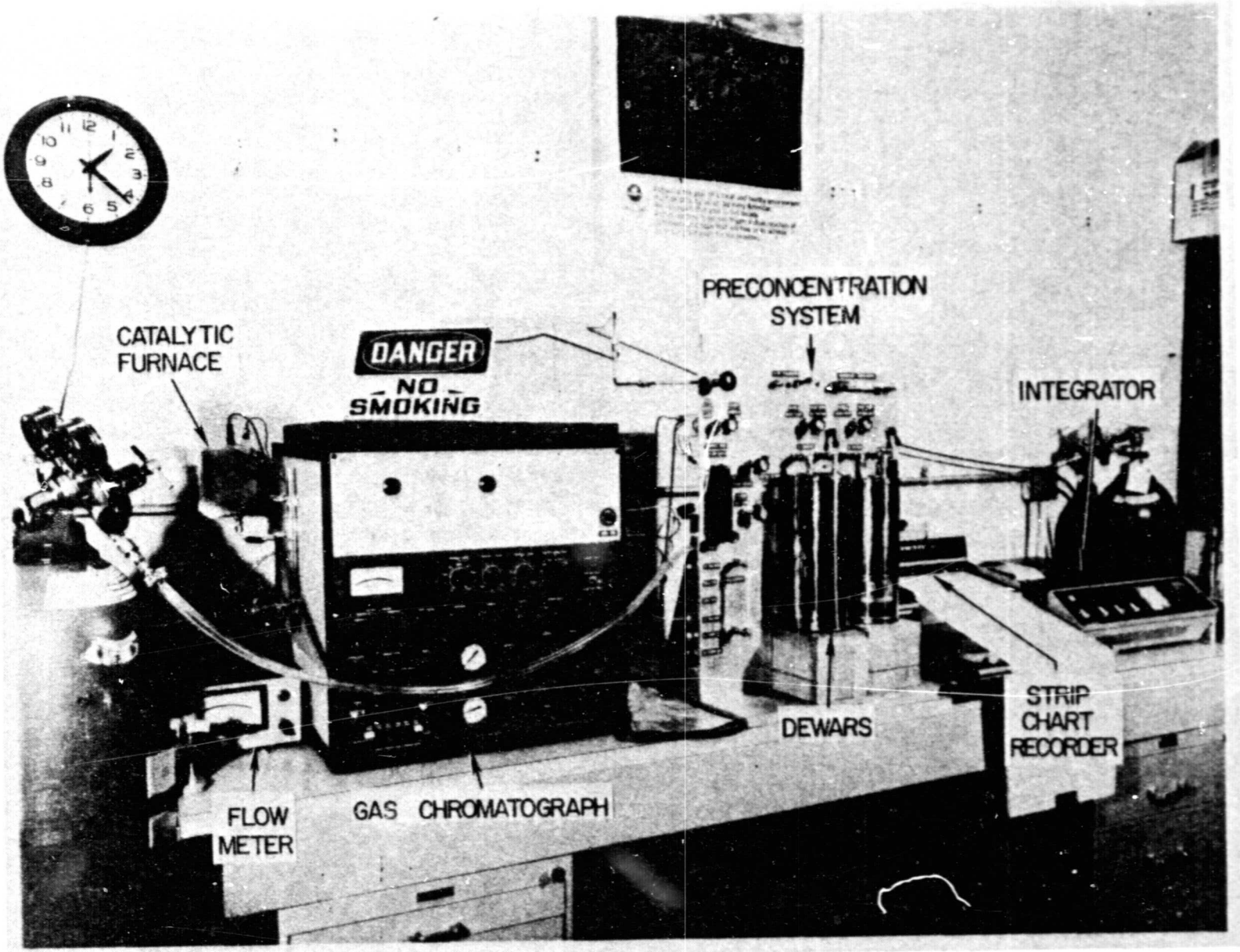

Figure 2. Photograph of the analysis system as operated in the laboratory.

THE MEASUREMENT SYSTEM

A. Description

The sample/calibration injection system consists of two sample loops: one, approximately 100 ml by volume is designated the air sampling loop, and the second loop, one ml by volume is the calibration loop. Figure 3 is a diagram of the plumbing of the sample loops and of the system of Carle 6 port valves (V1 through V6) which accomplish the air sampling and transfer from sample loops to traps and from traps to gas chromatograph.

One bottle of helium, the transfer helium, is plumbed to the cold trapping system and serves to transfer sample or calibration air from the sample loops to the cold traps by means of V1 or V3. Shown in figure 3 is the dual cold trapping system (two traps in series, T1 and T2) which preconcentrates the hydrocarbons heavier than CH_4 in the first trap and the CO and CH_4 in the second trap. Each cold trap is made of an aluminum tube 12 inches (30.48 cm) long × 1/4 inch (6.35 mm) O.D. formed into a 6 inch (15.24 cm) long U-tube filled with the appropriate adsorbent (column packing material). The tube containing activated alumina 42/60 mesh coated with 10 percent Nujol makes up the trap which removes CO_2, water, and all hydrocarbons heavier than CH_4; while the other tube containing a mixture of 1/4 activated charcoal 60/80 mesh to 3/4 (by weight) molecular sieve 5A 42/60 mesh makes up the trap which removes and holds the CH_4 and CO from the air sample.

Figure 3 also shows where two small scrubbers are plumbed into the system. One, a small glass tube 9.5 × 6.4 mm O.D. containing Mallcosorb, removes CO_2 from the calibration gas when the small 1-ml loop is used. Another glass tube 11 cm × 6.5 mm O.D. contains magnesium perchlorate, $Mg(ClO_4)_2$, and serves as a drying agent in the system.

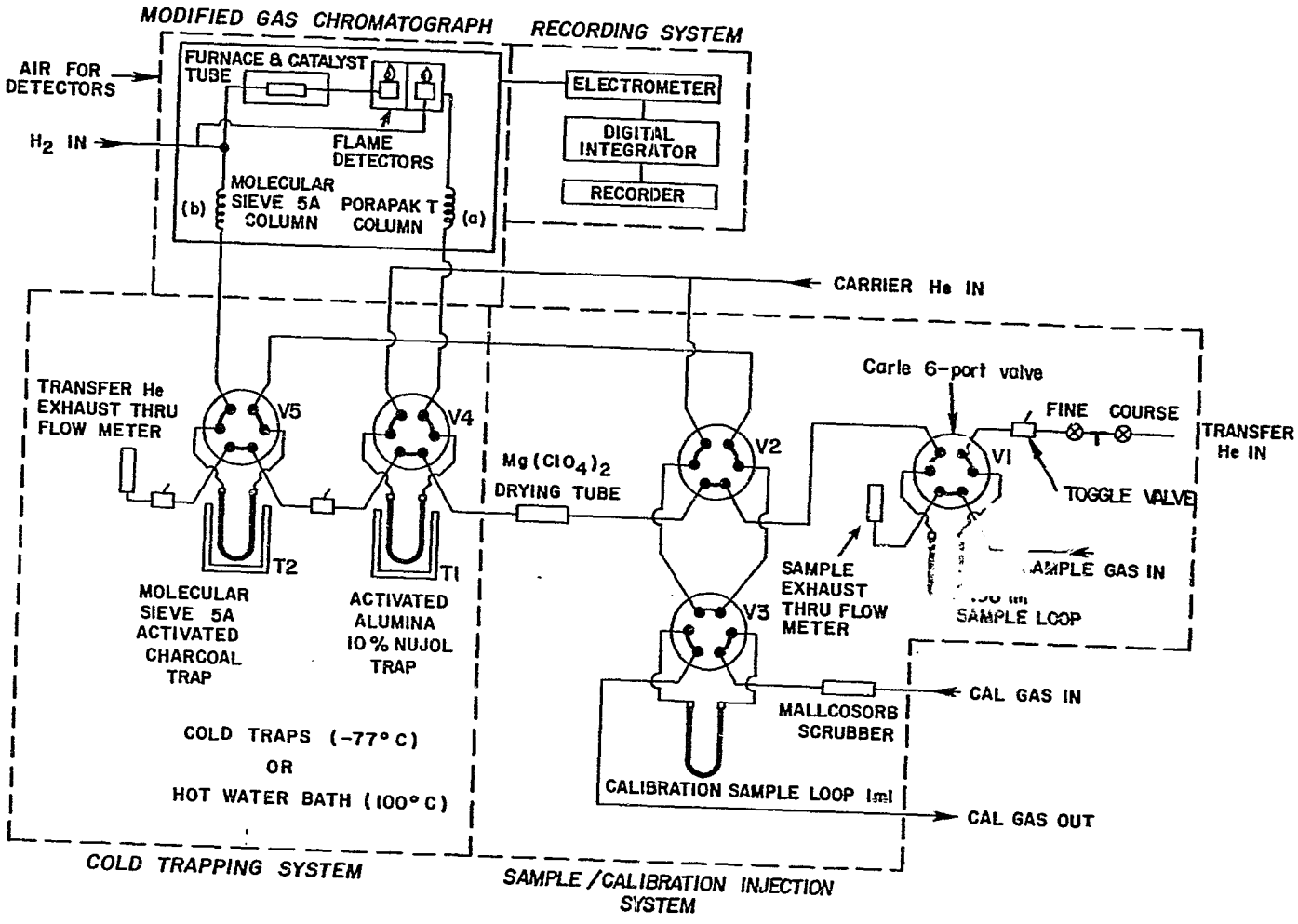

Figure 3. Diagram of the plumbing for the entire analysis system, showing the cold trapping system, and the gas chromatograph with the catalytic furnace.

A Varian model 2740 gas chromatograph equipped with dual flame ionization detectors is used for the analyses. A second helium source, the column helium, is plumbed to the chromatograph and transports the sample through the chromatograph column to the detectors. Inside the gas chromatograph, two columns are installed in parallel and operated at 60° C. The trap for hydrocarbons heavier than CH_4 is plumbed to the "a" side of the gas chromatograph. The "a" side has a 6-foot × 1/8-inch O.D. (183 cm × 3.2 mm) stainless steel column containing Porapak T which will separate the hydrocarbons heavier than methane in the air sample. The sample is transferred from trap T1 to column a by means of V4. The trap for CO and CH_4 is plumbed to the "b" side of the gas chromatograph which has a 6-foot × 1/4-inch O.D. (183 cm × 6.35 mm) stainless steel column containing molecular sieve 5A for separating CH_4 and CO. The "b" side of the chromatograph has been modified to include a nickel catalytic chamber at the column exit prior to the detector. The nickel catalytic chamber, operated at 325° C in a hydrogen atmosphere, converts the CO to CH_4 so that it may be measured by the flame ionization detector. The catalyst and its operation are described by Swinnerton, et al., in reference 4 and Porter and Volman in reference 5. The sample is transferred from trap T2 to column b by means of valve V5.

The data recording system includes a Varian CDS-101 digital integrator and a Varian A-25 strip chart recorder. The recorder has an accuracy of 0.25 percent full scale and a sensitivity of 1 μv. The chart grid size is a 10-inch maximum. The integrator is actually a microprocessor which can accept various parameter settings to calculate and, thus, compensate for background noise, baseline drift, and other chromatographic problems such as solvent peaks and fused peaks.

B. Operation

1. Analysis. During the usual analyses conducted with this system, air is transferred from the grab sample bottle to the 100-ml sample loop as per figure 4a. Prior to sample transfer, the traps T1 and T2 are cooled for approximately one minute by means of dry ice-acetone filled dewars. After the cool down period, sample gas from the 100-ml loop is moved through the two cold traps operated at -77° C by means of the transfer helium and valve V1 as shown in figure 4b. The first trap T1 (activated alumina with Nujol) removes CO_2, water, and all hydrocarbons heavier than CH_4 from the sample gas stream. The second trap, T2, (activated charcoal with molecular sieve) removes and holds the CO and CH_4 from the sample air. The remaining sample vents to the atmosphere along with the transfer helium. At this point, the traps are isolated by means of toggle valves, the dry ice-acetone baths are removed, and 100° C water baths are used to heat the traps and desorb the gases present. A valve change, V4 and/or V5, occurs and the column helium transports the gases from the traps through the respective column as shown in figure 4c.

The nonmethane hydrocarbons held on the first trap may be analyzed on the Porapak T column attached to the "a" side of the chromatograph. Currently, this capability is not being utilized, but plans are to expand the measurement effort to include the C_1 to C_4 hydrocarbons. The CO and CH_4, after separation on the "b" column containing molecular sieve, pass through a nickel catalytic chamber attached to the gas chromatograph. The CO is converted to methane in the catalytic chamber and measured as methane by the flame ionization detector (FID) of the chromatograph. The ambient air methane contained in the same sample passes through the catalytic chamber unreacted

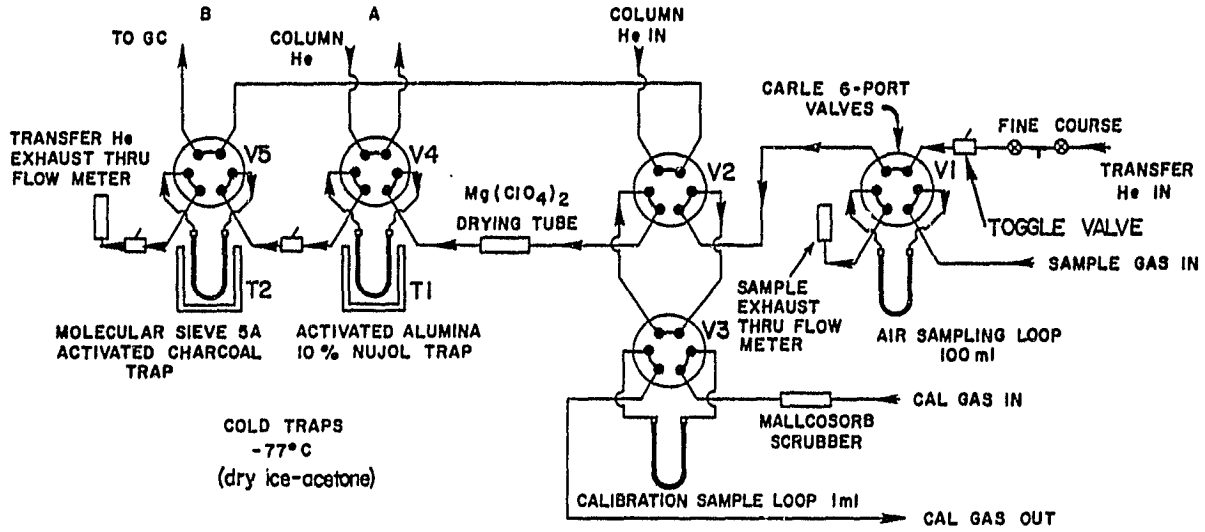

Figure 4a. Valve diagram for cold trapping system showing transfer helium purging cold traps while sample gas fills sample loop or calibration gas fills the calibration loop.

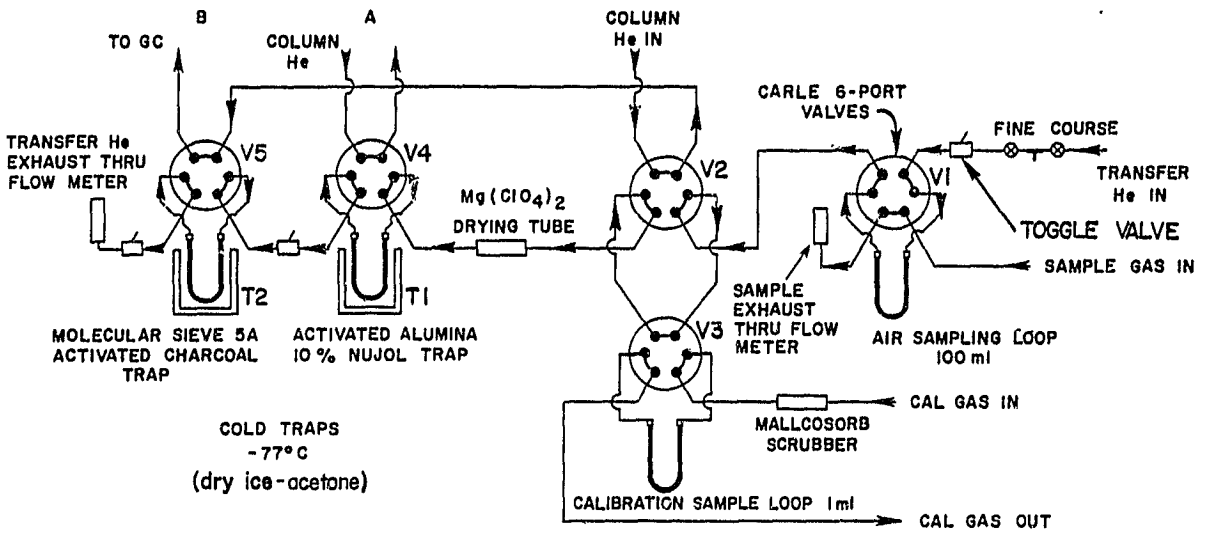

Figure 4b. Transfer helium moving sample from the 100 ml loop through the cold traps.

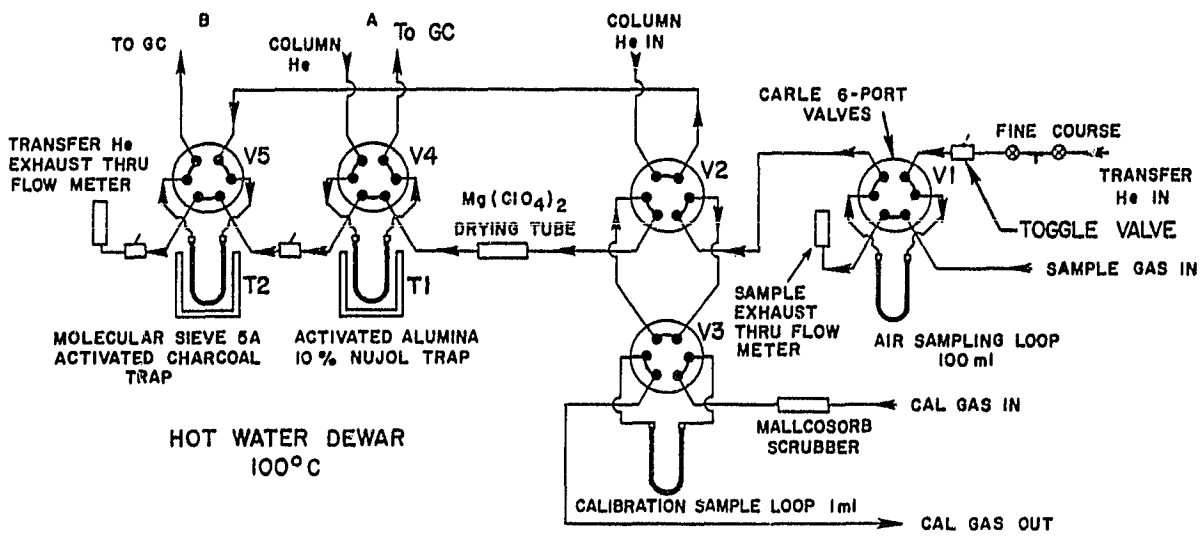

Figure 4c. Column helium pushing gas from each trap onto the respective gas chromatograph column.

and is also measured by the FID. The signal from the FID is plotted on a strip chart recorder as shown in figure 5, and peak area is computed by the digital integrator.

2. Calibration. The small loop is used to perform a quick calibration of the gas chromatograph and catalyst system. When necessary, the small loop may also be used for sampling high ambient levels of CO which might otherwise saturate the cold trap. Gas from the small loop may be directed through the trapping system or it may be sent directly into the gas chromatograph via valve V2, as shown in figures 4d and 4e. When the sample from the small loop is injected directly into the chromatograph, the small loop serves only to calibrate the "b" side of the chromatograph (to which the catalytic furnace is attached). The sample from the small loop cannot be injected directly into the "a" side through the cold traps. The gas concentration used in the small loop is significantly higher than that used in the large loop in order that approximately the same signal level is seen by the detector in either case. Concentrations range from 10 to 100 ppm when the small loop is used for a calibration.

Calibration may also be accomplished using the 100-ml loop. Since sample preconcentration (use of the cold traps) always takes place when the large loop is used, the calibration standard need contain only a few ppm or less of the gas interest, when the calibration is performed in this way. Commercially available gas standards of known concentration are used to calibrate the system. These standards, which in the past were shown to be unstable at the low concentrations representative of ambient levels, are now available in special aluminum cylinders. Gases in these special cylinders have been shown to be stable for extended periods of time of up to a few years. The gas standards now used to calibrate this measurement system are purchased in these special aluminum tanks.

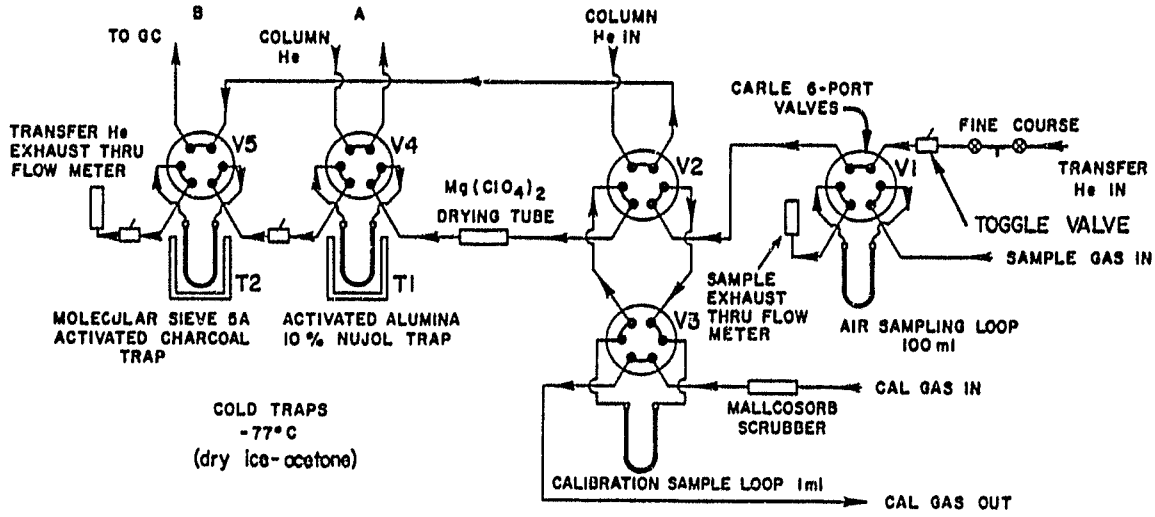

Figure 4d. Transfer helium moving gas from 1 ml calibration loop through the cold traps.

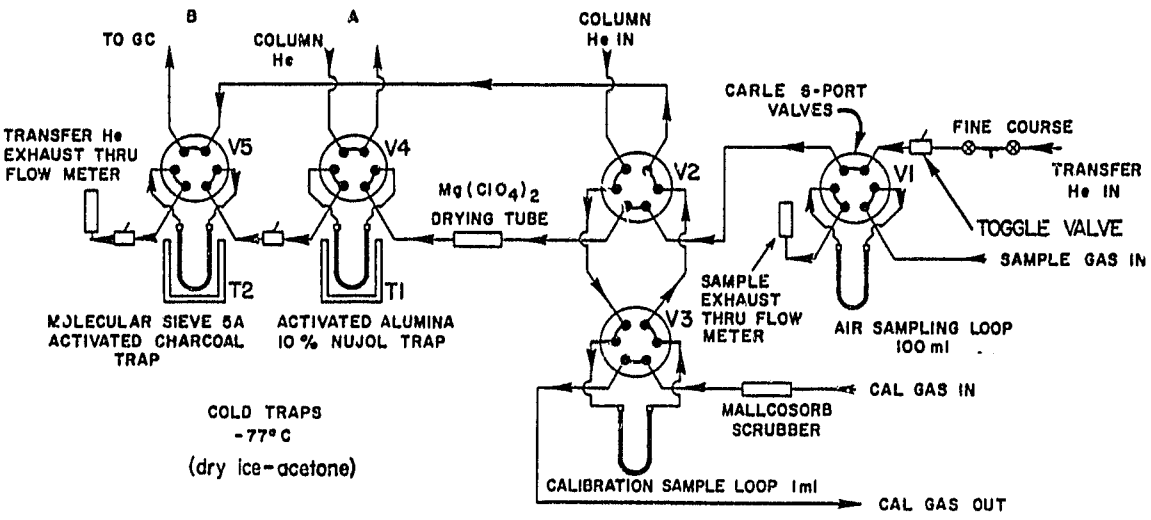

Figure 4e. Gas from calibration loop injected directly into the "b" side of the gas chromatograph.

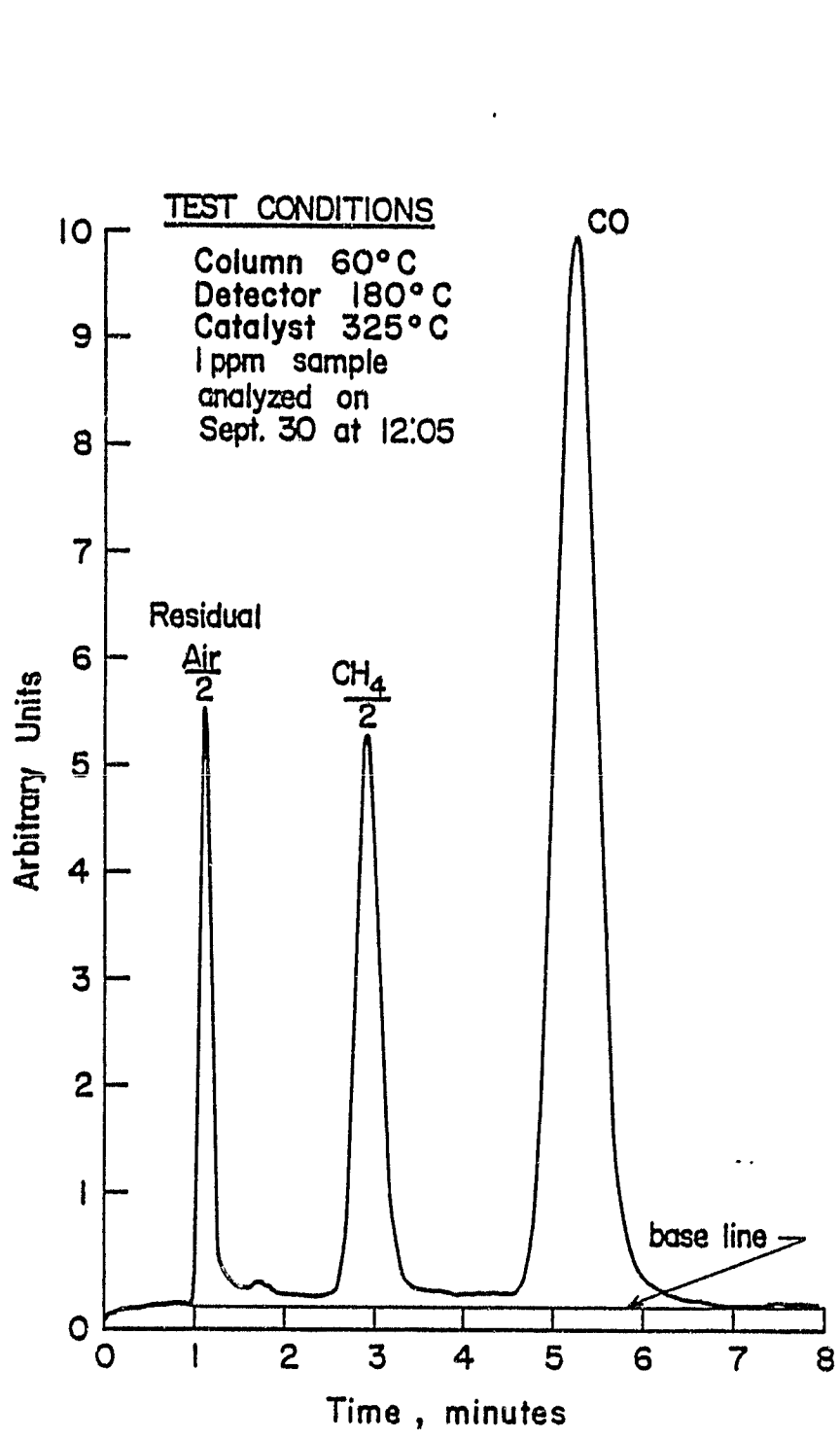

Figure 5. Typical chromatogram obtained with the measurement system when a calibration standard of 1 ppm is used.

C. Data Reduction

The data from the gas chromatograph are read out on a Varian model A-25 strip chart recorder. Peak areas are computed by the Varian CDS-101 integrator. Figure 5 is a typical chromatogram.

Standards of known concentration are analyzed and the peak area for each individual component is computed automatically by the integrator. The peak area is directly proportional to the amount of pollutant gas present in the air sample. A graph of area versus known concentration is plotted and the unknown concentrations of the ambient air samples are then read directly from the calibration plot.

The measurement precision has been shown to be approximately one percent by analyzing the same calibration gas (at the 1 ppmv CO level) repeatedly throughout the day. Noise equivalent concentration is $\leq$ 5 ppb for CO. The system can only be as accurate as the gas standards used for its calibration. The gas standards currently used are provided with an analysis of the contents of each cylinder. The nominal analytical accuracy or deviation of value is given by the manufacturers as ±2 percent of the value reported in their analysis of the contents of the bottle.

SAMPLE BOTTLES

Since the above described system (as well as other existing laboratory equipment) is not suitable as flight hardware, a sample bottle program is being conducted to determine the CO distribution in the ambient atmosphere. Sample bottles can readily be used for inflight sampling, as well as ground sampling. The containers currently in use are commercially available from Whitey Company of

Oakland, California. They are seamless bottles spun of 304 stainless steel and 300 ml by volume.

Difficulty with erratic data from the bottle samples led to the development of a cleaning and heat treatment process for the stainless steel bottles. The procedure was as follows: the bottles were first degreased in trichloroethylene overnight. They were then placed in a vacuum furnace at 10^{-4} torr and heated to 1010° C. The temperature was held there for five minutes, and then the bottles were allowed to cool gradually to room temperature while still under vacuum. This process was used to degrease and outgas the bottles to remove any oil film or oil residues that may have collected and contaminated the inside of the bottle during manufacture. Figure 6 is a photograph of a rack of ten stainless steel bottles as they are flown on the aircraft.

Difficulty with the erratic data also led to investigations into the use of glass bottles for ambient air sampling. Glass had not been considered for sampling purposes orginally because it is fragile and presents a safety problem in handling. However, it was thought that this safety problem could be overcome so 20 pyrex glass bottles were purchased from Fisher Scientific and were modified by the NASA/Langley glass shop to accept brass bellows valves. The valves (B4H) were manufactured by Nupro Company of Cleveland, Ohio. Two racks of 10 bottles each were then fabricated by permanently foaming the bottles in place using a polyurethane foam. The foam, Isofoam PE-2, not only separates and holds the individual bottles, but it serves to eliminate any hazard from possible breakage of the glass while the bottles are being used. Since each bottle is entirely encased by the foam, there is no danger of flying glass in case of either implosion or explosion of any bottle.

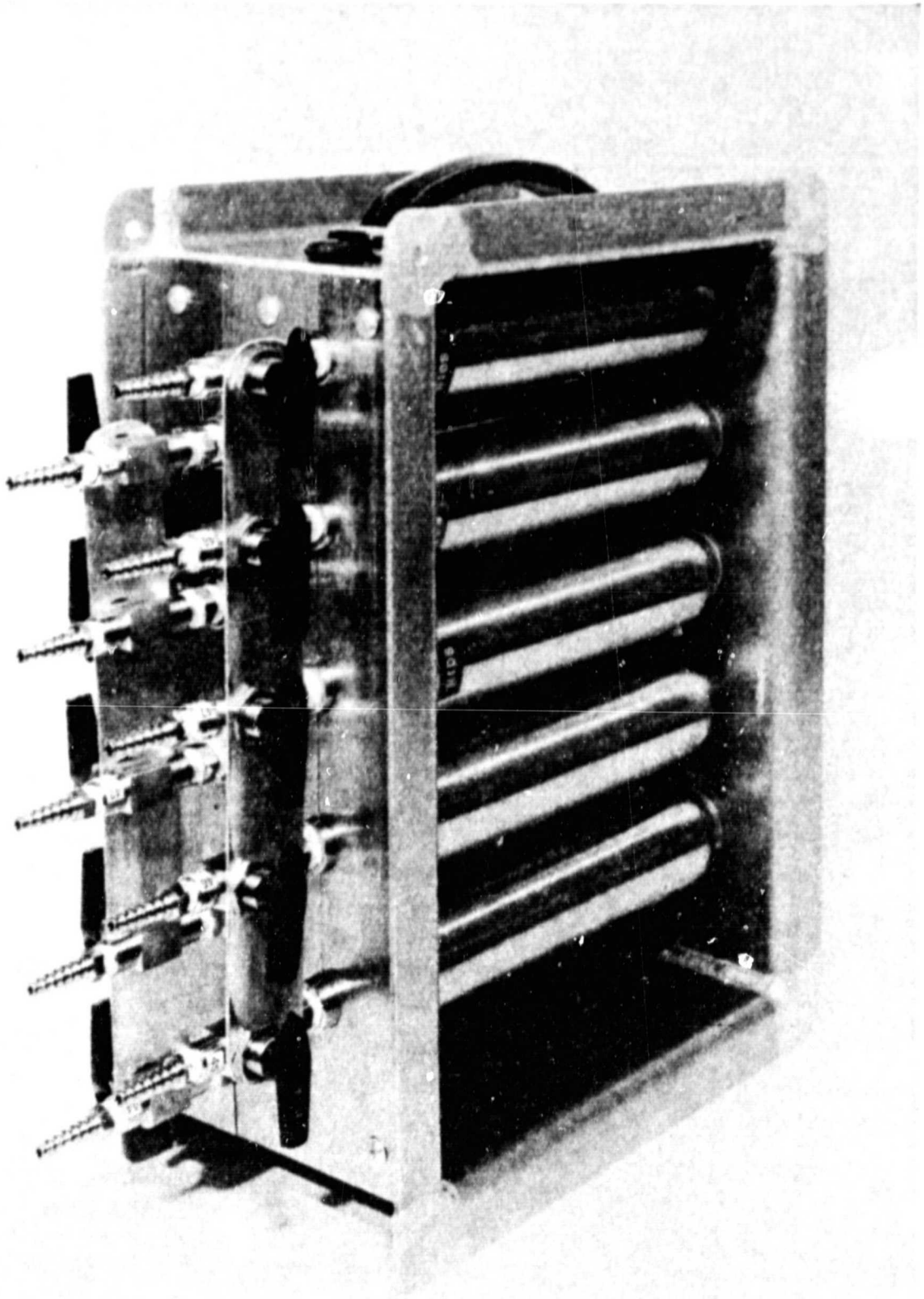

Figure 6. Photograph of a rack of the stainless steel bottles as they are flown on the aircraft.

Results from studies on the glass bottles indicate that the measurement accuracy may be improved by their use. Repeatability studies indicate that the data scatter for the stainless steel bottles is about 7 percent, but the data from the stainless bottles averages about 10 percent higher than the true value. The glass bottles show about a 10 percent scatter, but there is no bias in the data from the true value when the glass bottles are used.

SUMMARY AND CONCLUSIONS

An analytical system has been developed for the measurement of the trace atmospheric gases methane and carbon monoxide. The system incorporates sample preconcentration and a gas chromatographic technique that uses catalytic conversion of CO to CH_4. The method is of sufficient sensitivity and repeatability to obtain the concentrations of methane and carbon monoxide at clean air levels. A bottle sampling program is also being conducted for use with the described measurement system to define concentration profiles for CH_4 and CO in the planetary boundary layer. The data obtained from this program are being used to develop a characterization of the continental CO distribution.

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